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PRODUCTION AND CURING OF POLYMERS CONTAINING TERMINALLY REACTIVE NITROGEN

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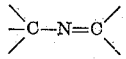
This invention relates to a method of preparing a polymer having terminal groups containing reactive nitrogen and to the curing of such polymer to produce a product having either a linear or crosslinked structure. In another aspect, this invention relates to the polymeric products thus produced.

It has been disclosed in copending application, Serial No. 772,167, of Uraneck, Short, Hsieh and Zelinski, filed November 6, 1958, now Patent Number 3,135,716, that highly useful polymeric products can be obtained by polymerizing vinylidene-containing monomers in the presence of an organo alkali metal catalyst and subsequently reacting the resulting polymer containing active alkali metal end groups with a reagent which will couple the polymer molecules or replace the alkali metal atoms with more stable reactive end groups. The utilization of these reactive terminal substituents on the polymer molecule enables substantially more effective cures since all the molecules can be tied into a crosslinked structure. Also, by simple coupling arrangements alone or with auxiliary curing, liquid polymers can be readily converted to solids and soft tacky rubber can be made quite rigid.

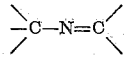
The term "telechelic" has been coined to define terminally reactive polymers which contain a reactive group on two or more ends of the polymer molecule. As used in this specification and in the claims, telechelic polymers means polymers of vinylidene-containing monomers which contain a reactive group on each end of the polymer molecule. The term "semi-telechelic" can be used to designate those polymers which contain a reactive group on only one end of the polymer molecule. When referring to terminally reactive polymers, it is intended that both telechelic and semi-telechelic polymers be included.

According to our invention, a process is provided for preparing polymer which comprises reacting a polymer of a vinylidene-containing monomer, said polymer containing at least 1 terminally positioned alkali metal atom per molecule, with a non-polymerizable compound containing the structure



After removing the alkali metal atoms from the resulting polymer, this polymer can be coupled and/or cured by treatment of the reactive terminal groups with a polyhalogen-containing compound and crosslinked at intervals along the polymer chain with conventional curatives. Our invention, therefore, provides a method of converting liquid polymers to solid products and solids to higher molecular weight materials. The polymer containing the terminally positioned alkali metal atom can be prepared by polymerizing vinylidene-containing monomer in the presence of an organoalkali metal initiator such as, for example, a compound $R(Li)_x$ where x is 1 to 4 and R is an aliphatic, cycloaliphatic or aromatic radical of 1 to 20 carbon atoms.

According to another aspect of our invention, a polymer containing a terminally reactive alkali metal atom is reacted with a compound containing at least 2 of the groups



The resulting polymer can then react with still another polymer containing a terminally positioned alkali metal atom to produce a coupling arrangement in which the molecular weight of the polymer is substantially doubled without entering into any crosslinking. This product can then be cured with a polyhalogen-containing compound by reacting such compound with the reactive nitrogen positioned either at the ends of the polymer molecule or at the points of coupling.

It is an object of our invention to provide a method of preparing polymers which contain terminally reactive nitrogen. It is another object of our invention to provide a method of preparing and curing polymers which contain terminally reactive nitrogen to produce a product which has either a linear or crosslinked structure. Another object is to provide a method of coupling polymers containing terminally reactive alkali metal atoms to produce a product which has reactive nitrogen at the points of coupling which can subsequently be linked to other polymer molecules through halogen-containing compounds. Another object of our invention is to produce a polymer which contains terminally reactive nitrogen, said polymer being curable with polyhalogen-containing compounds and, further, to produce a compounded polymeric product which has been cured both with conventional curatives and with polyhalogen-containing compounds. Other objects, advantages and features of our invention will be apparent to those skilled in the art from the following discussion.

The monomers which can be employed in the preparation of polymers containing terminal alkali metals include conjugated dienes and vinyl-substituted aromatic compounds. The preferred monomers are the conjugated dienes containing from 4 to 12 carbon atoms and preferably 4 to 8 carbon atoms per molecule. The conjugated dienes include

1,3-butadiene,
isoprene,
2,3-dimethyl-1,3-butadiene,
1,3-pentadiene (piperylene),
2-methyl-3-ethyl-1,3-butadiene,
3-methyl-1,3-pentadiene,
2-methyl-3-ethyl-1,3-pentadiene,
2-ethyl-1,3-pentadiene,
1,3-hexadiene,
2-methyl-1,3-hexadiene,
1,3-heptadiene,
3-methyl-1,3-heptadiene,
1,3-octadiene,
3-butyl-1,3-octadiene,
3,4-dimethyl-1,3-hexadiene,
3-n-propyl-1,3-pentadiene,
4,5-diethyl-1,3-octadiene,
phenyl-1,3-butadiene,
2,3-diethyl-1,3-butadiene,
2,3-di-n-propyl-1,3-butadiene,
2-methyl-3-isopropyl-1,3-butadiene,

and the like. Conjugated dienes containing alkoxy substituents along the chain can also be employed, such as 2-methoxy-1,3-butadiene, 2-ethoxy-3-ethyl-1,3-butadiene, and 2-ethoxy-3-methyl-1,3-hexadiene. Conjugated dienes can be polymerized alone or in admixture with each other to form copolymers or block copolymers. Block copolymers can be prepared from two or more conjugated dienes by charging one compound initially, allowing it to polymerize, and then adding a second conjugated diene, etc.

The vinyl-substituted aromatic compounds include styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, and alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkoxy, aryloxy, and dialkylamino derivatives thereof in which the total number